



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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In re Application of: :

Kimiyuki Ito et al.

Art unit: 1756

Serial No.: 09/955,030 :

Filed: September 19, 2001

For: PHOTSENSITIVE MEMBER :

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DECLARATION

Honorable Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

Sir:

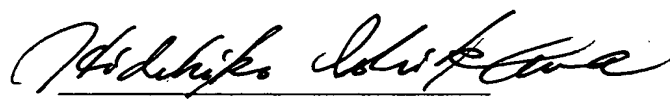
I, Hidehiko Ishikawa hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 203087/1995.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize

the validity of the above-identified application or any patent  
issuing thereon.

A handwritten signature in cursive script, appearing to read "Hidehiko Ishikawa", written in black ink.

Hidehiko ISHIKAWA

Dated: This *24*th day of *February*, 2007.



[Name of Document] Patent Application

[Reference Number] 147954

[Date of Presentation] August 9th in the 7th year of the  
Heisei Era (1995)

[Address] Director-General of the Patent Office

[International Patent Classification] G03G 5/147

[Title of Invention] Photosensitive Member

[Number of Claims] 1

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[Payment Amount] 21000

[List of Presented Articles]

[Article Name] Specification 1

[Article Name] Abstract 1

[Number of Power of Attorney] 9201586

[Name of document] Specification

[Title of the Invention] PHOTSENSITIVE MEMBER

[Scope of claims]

[Claim 1] A photosensitive member comprising, on the uppermost surface, a layer comprising tantalum-doped tin oxide powder in a resin.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Relates] The present invention relates to an electrophotographic photosensitive member, and more specifically to a photosensitive member comprising a protective overcoat layer on a photosensitive layer.

[0002]

[Conventional Technologies] In order to minimize abrasion and enhance durability, a protective layer is commonly formed on the surface of a photosensitive layer, particularly the surface of an organic-based photosensitive layer. The photosensitive member is subjected to repeated charging and image exposure. Consequently, to minimize accumulation of charge on the surface of the protective layer or the interior, a protective layer is required to provide lower insulation. However, if conductivity is too high, unsharp images are formed due to charge migration in the lateral direction. On the contrary, when the conductivity is too low, fogging results on images due to charge accumulation. Therefore,

conductivity of the protective layer should be controlled within an appropriate value, and further, the specified conductivity should be maintained against external effects such as temperature or humidity.

[0003] Further, in order to protect from damage due to a toner cleaning blade and the like, the protective layer must be capable of satisfying desired mechanical strength.

[0004] Further, the protective layer should not adversely affect the spectral sensitivity of the photosensitive member due to coloring via the addition of materials to lower insulation.

[0005] In view of the foregoing, employed as a protective layer is one in which conductive powder is dispersed in a binder resin. For example, Japanese Unexamined Patent Application No. SHO 56-138742 discloses a protective layer containing antimony-doped tin oxide as conductive fine particles dispersed in a resin.

[0006]

[Problems to be Solved by the Invention] In view of the foregoing, the present invention was achieved. An object of the present invention is to provide, as an uppermost layer of the photosensitive member, a novel layer, in which conductive tantalum-doped tin oxide which results in no environmental pollution and exhibits excellent safety, is dispersed in a resin.

[0007] Another object is to provide a photosensitive member

which exhibits excellent characteristics such as high sensitivity, can form excellent images without image unsharpness and fogging and the like, and exhibits excellent repetition characteristics and durability.

[0008]

[Means to Solve the Problems] The present invention relates to a photosensitive member which incorporates, on the uppermost surface, a layer (hereinafter, referred to as a "dispersion layer") which contains tantalum-doped tin oxide powder in a resin.

[0009] The tantalum-doped tin oxide ( $\text{SnO}_2$ ) used in the present invention is a tin oxide doped with 0.1 to 10 percent-by-weight tantalum metal. The doping may be accomplished by forming a solid solution of tin oxide and tantalum, or coating the surface of the tin oxide with tantalum. Doping may be also accomplished by fusing the tantalum to the tin oxide.

[0010] In the present invention, tin oxide is doped with tantalum and subsequently, a surface treatment is conducted with a silane coupling agent, a titanium coupling agent or the like. By using such as the above, it is possible to further enhance the dispersibility of an application fluid and to enable the formation of a uniform coating. Further, it is possible to further enhance moisture resistance via the coupling treatment.

[0011] The used tantalum-doped tin oxide has a mean particle size equal to or less than 2  $\mu\text{m}$ , and preferably equal to or less than 1  $\mu\text{m}$ , but more preferably 0.3 to 1.0  $\mu\text{m}$ . When the particle size is too large, cleaning properties are degraded due to passage of toner particles, while when it is too small, it becomes difficult to uniformly disperse particles in a layer, causing insufficient cleaning.

[0012] Tantalum-doped tin oxide is incorporated in the dispersion layer in a amount of 5 to 70 percent-by-weight with respect to the entire dispersion layer, but is preferably 7 to 40 percent-by-weight. When the content is too small, abrasion resistance and scratch resistance become insufficient, and the residual potential as a photosensitive member is elevated. On the other hand, when the content is too large, minute irregularities are formed on the surface of the finished protective overcoat layer, resulting in lowered toner cleaning properties, whereby passage of toner particles becomes problematic. Further, degradation of photosensitivity characteristics due to lowered translucency and decrease in mechanical strength also become problematic.

[0013] Formed under the dispersion layer is a photosensitive layer. The photosensitive layer is structured by suitably selected materials known in the art, such as charge generating materials, charge transporting materials or binder resins. The above materials may be applied to any laminated layer type photosensitive layer in which a charge



transporting layer is applied onto a charge generating layer, being a so-called reverse laminated layer type photosensitive layer in which a charge generating layer is provided on a charge transporting layer, and the so-called single layer structured photosensitive layer which exhibits both a charge generating function and a charge transporting function.

[0014] Further, other than organic photosensitive layers, employed may be layers using inorganic materials such as zinc oxide, cadmium sulfide, a selenium based alloy, an amorphous silicon based alloy or the like.

[0015] A case will now be described in which, as the photosensitive member of the present invention, a photosensitive member is produced in such a manner that a charge generating layer, a charge transporting layer, and the dispersion layer of the present invention are sequentially laminated.

[0016] Examples of useful substrates include conductive foil or plates of copper, aluminum, iron, nickel and the like in a sheet-like or drum-like configuration. Further useful substrates include resin films and the like that are subjected to vacuum deposition or electroless plating with the metal described above, or paper or resin films on which are formed conductive compounds layers including indium, oxide, tin oxide and the like by coating or deposition as well. A member, imparting conductivity by forming a conductive layer according the present invention, as

previously described, on the surface of a material, which lacks conductivity, such as insulated resin film, paper, and the like, may be used as a substrate of the present invention.

[0017] A charge generating layer is formed on the aforesaid substrate. The charge generating layer is formed in such a manner that charge generating materials are subjected to: vacuum deposition; are dissolved in an appropriate solvent and coated; or an application fluid, prepared by dispersing pigment into an appropriate solvent or if desired, into a solution incorporating binder resins, is coated followed by drying. Onto the resulting layer, applied is a solution incorporating a charge transporting material and a binder resin, followed by drying, whereby a charge transporting layer is formed.

[0018] Examples of charge generating materials usable for the photosensitive member of the present invention include: bisazo pigments, triarylmethane dyes, thiazine dyes, oxazine dyes, xanthene dyes, cyanine pigments, styryl pigments, pyrylium dyes, azo dyes, quinacridone dyes, indigo pigments, perylene pigments, polycyclic quinone pigments, bisbenzimidazole pigments, indathrone pigments, squarylium pigments, phthalocyanine pigments and the like. Any materials may be used insofar as said materials generate charge carriers and are extremely efficient in light absorption.

[0019] Further employed as charge transporting materials,

used in the photosensitive member, described as above, may be various compounds such as hydrazone compounds, pyrazoline compounds, styryl compounds, triphenylmethane compounds, oxadiazole compounds, carbazole compounds, stilbene compounds, enamine compounds, oxazole compounds, triphenylamine compounds, tetraphenylbenzidine compounds, azine compounds or the like.

[0020] Binder resins used to produce the photosensitive member, described as above, exhibit electric insulation, and their volume resistivity, when individually determined, is preferably at least  $1 \times 10^{12} \Omega \cdot \text{cm}$ . For example, used may be binder materials known in the prior art, such as thermoplastic resins, thermosetting resins, photocuring resins, photoconductive resins or the like. Specific examples include: thermoplastic resins such as saturated polyester resins, polyamide resins, acrylic resins, ethylene-vinyl acetate resins, ion-crosslinked olefin copolymers (being ionomers), styrene-butadiene block copolymers, polycarbonate, vinyl chloride-vinyl acetate copolymers, cellulose ester, polyimide, styrol resins, or the like; thermosetting resins such as epoxy resins, urethane resins, silicone resins, phenol resins, melamine resins, xylene resins, alkyd resins, thermosetting acrylic resins or the like; photocuring resins; and photoconductive resins such as polyvinyl carbazole, polyvinyl pyrene, polyvinyl anthracene, polyvinyl pyrrole or the like. These binder resins may be

used individually or in combinations of at least two types.

[0021] Incidentally, when the charge transporting material itself is a polymer charge transporting material usable as a binder, other binder resins need not be used.

[0022] In the photosensitive member of the present invention, together with the binder resin, employed may be plasticizers such as halogenated paraffin, polychlorinated biphenyl, dimethylnaphthalene, dibutyl phthalate, O-terphenyl or the like, electron attractive sensitizers such as chloranil, tetracyanoethylene, 2,4,7-trinitrofluorenone, 5,6-dicyanobenzoquinone, tetracyanoquinodimethane, tetrachlorophthalic anhydride, 3,5-dinitrobenzoic acid or the like, and sensitizers such as methyl violet, rhodamine B, cyanine dyes, pyrylium salts, thiapyrylium salts or the like.

[0023] The dispersion layer in the uppermost surface of the photosensitive member is formed in such a manner that tantalum-doped tin oxide powder is dispersed in a binder resin solution, to be described below, and the resulting dispersion is applied onto the surface of a carrier transporting layer, and subsequently dried. It is desirable that after application, drying is accomplished in a temperature range of 60 to 120 °C. Any appropriate resin may be used to structure the dispersion layer insofar as said resin satisfies certain conditions such as sufficient solvent resistance, excellent powder dispersibility, and the like. Examples of useful well known materials include: polyvinyl

alcohol, polyvinyl methyl ether, poly-N-vinyl imidazole, ethyl cellulose, methyl cellulose, ethylene-acrylic acid copolymers, casein, gelatin, polyamide, and the like.

Examples of typical useful resins include: thermoplastic resins, such as polyester resins, acrylic resins, vinyl acetate resins, vinyl chloride-acetate resins, polyvinyl butyral resins, and the like, as well as thermosetting resins, such as alkyd resins, melamine resins, urethane resins, epoxy resins, phenolic resins and the like. Of the aforesaid resins, in view of adhesion and application characteristics, particularly preferred are polyester resins, acryl-melamine resins, urethane resins and the like.

[0024] Usable methods to apply the dispersion layer onto the substrate include a dip coating method, a spray coating method, a spinner coating method, a wire bar coating method, a blade coating method, a roller coating method, a curtain coating method and the like.

[0025] The thickness of the dispersion layer is controlled to be equal to or less than 7  $\mu\text{m}$ , but is preferably 1 to 5  $\mu\text{m}$ . It is possible to form a relatively thick dispersion layer of the present invention, whereby durability of the photosensitive member is enhanced.

[0026] A case is described in which the charge generating layer, the charge transporting layer, and the dispersion layer of the present invention are sequentially formed on a substrate. It is possible to apply in the same manner to a

photosensitive member of the other structure. Further, appropriate modification may be made to match the embodiment of each of the photosensitive members.

[0027] As mentioned above, it is possible to make the thickness relatively thick, whereby in the present invention, the photosensitive member, in which the aforesaid dispersion layer is formed on the organic photosensitive layer, is most useful in terms of enhancement of durability.

[0028] Further, in order to improve charging property, image quality, adhesion property and the like, the photosensitive member of the present invention may be provided with an undercoat layer under the photosensitive layer. Usable materials of the above undercoat layer include: resins such as ultraviolet radiation hardening resins, normal temperature hardening resins, or heat hardening resins, mixed resins which are prepared by dispersing a resistance controlling material into the above resins, thin vacuum layer materials which are prepared in such a manner that metal oxides, metal sulfides or the like are modified into a thin layer, employing a deposition method an ion plating method under vacuum or the like, as well as amorphous carbon film, amorphous silicon carbide film or the like, prepared via a plasma polymerization method.

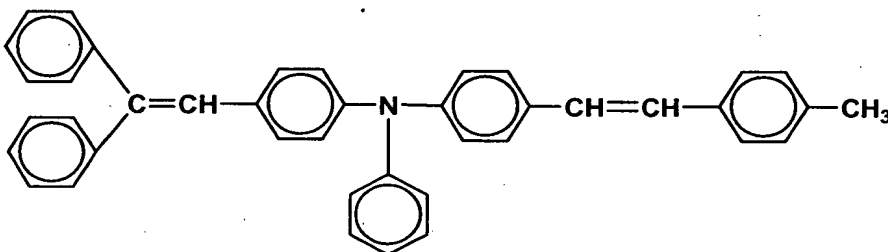
[0029]

[Examples]

Example 1

By employing a sand mill, 1 part-by-weight (hereinafter pbw)  $\tau$  type metal-free phthalocyanine, 0.5 pbw polyvinyl butyral, and 50 pbw tetrahydrofuran (THF) were dispersed. The obtained phthalocyanine based dispersion fluid was applied onto an aluminum drum to form a layer thickness after drying of 0.3  $\mu\text{m}$  to form a charge generating layer.

[0030] An application fluid, prepared by dispersing 10 pbw distyryl compound represented by the following formula:



and 12 pbw polycarbonate resin (TS2020, produced by Teijin Chemicals Ltd.) into 180 pbw tetrahydrofuran, was applied onto the aforesaid charge generating layer and subsequently dried, whereby a 22  $\mu\text{m}$  thick charge transporting layer was formed.

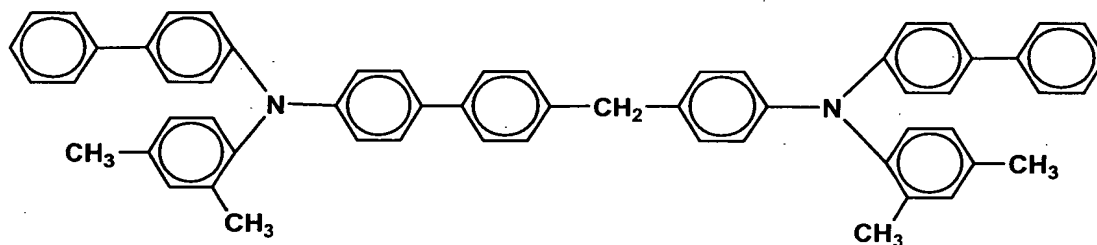
[0031] An application fluid prepared by dispersing 40 pbw tantalum-doped tin oxide ( $\text{SnO}_2$ ) (PASSTRAN TYPE-VI, produced by Mitsui Mining and Smelting Co., Ltd) into 70 pbw polyurethane solution (RETAN 4000, produced by Kansai Paint Co., Ltd.) was applied onto the aforesaid charge transporting layer to reach a thickness after drying of 2  $\mu\text{m}$  and subsequently dried, whereby a photosensitive member was

produced.

[0032] Example 2

By employing a sand mill, 1 pbw  $\tau$  type metal-free phthalocyanine, 0.5 pbw polyvinyl butyral, and 50 pbw tetrahydrofuran (THF) were dispersed. The obtained phthalocyanine based dispersion fluid was applied onto an aluminum drum to reach a layer thickness after drying of 0.3  $\mu\text{m}$  to form a charge generating layer.

[0033] An application fluid prepared by dispersing 10 pbw benzyldiphenyl compound represented by the following formula:



and 10 pbw polycarbonate resin (PANLITE K-1300, produced by Teijin Chemicals Ltd.) into 180 pbw dichloromethane was applied onto the aforesaid charge generating layer and subsequently dried, whereby a 25  $\mu\text{m}$  thick charge transporting layer was produced.

[0034] An application fluid prepared by dispersing 30 pbw tantalum-doped tin oxide ( $\text{SnO}_2$ ) (PASSTRAN TYPE-VI, produced by Mitsui Mining and Smelting Co., Ltd.) into 60 pbw acrylic resin solution (G-4663A, produced by No-Tape Industrial Co., Ltd.) was applied onto the aforesaid charge transporting layer to reach a thickness of the layer after drying of 3 mm and subsequently dried, whereby a photosensitive member was



produced.

[0035] Reference Example 1

A photosensitive member was produced in exactly the same manner as Example 1, with the exception that tantalum-doped tin oxide was not incorporated in the protective overcoat layer.

[0036] Reference Example 2

A photosensitive member was produced in exactly the same manner as Example 2, with the exception that in Example 2, a tin oxide powder, which was not tantalum-doped, was used.

[0037] Each of the photosensitive members, obtained in Examples 1 and 2 and Reference Examples 1 and 2, was installed in a printer (SP101, produced by Minolta Co., Ltd.). Printing durability was tested employing 5,000 (hereinafter 5K) sheets. For each photosensitive member, at the beginning and after 5K, exposure quantity (hereinafter half decay exposure)  $E_{1/2}$  (erg/cm<sup>2</sup>) required to decay the initial surface potential  $V_0$  (V) to half its value, and the decay rate  $DDR_1$  (%) of the initial potential when stored in a dark place for one second were measured. The produced images were visually examined and ranked as below. Further, the amount shaving of the protective overcoat layer after 5K was measured and ranked as below.

[0038] Image Evaluation:

O: No fog or unsharp images was observed

X: Light density, and some fog and unsharpness observed

[0039] Shaved Amount

O: shaved amount was equal to or less than 1  $\mu\text{m}$

X: shaved amount exceeded 1  $\mu\text{m}$

[0040] Table 1 summarizes the above results.

[0041]

Table 1

	E <sub>1/2</sub> (erg/cm <sup>2</sup> )		Image		Shaved Amount	V <sub>0</sub> (V)		DDR <sub>1</sub> (%)	
	Initial	After 5K	Initial	After 5K		Initial	After 5K	Initial	After 5K
Example 1	2.5	2.6	0	0	0	-750	-750	3.3	3.8
Example 2	2.7	2.9	0	0	0	-760	-750	3.6	3.8
Reference Example 1	4.5	9.8	X	X	X	-770	-780	2.5	2.9
Reference Example 2	3.1	5.6	0	X	0	-760	-770	3.1	4.3

**[0042]**

[Effects of the Invention] The present invention provides a photosensitive member capable of maintaining stable photosensitive member characteristics such as sensitivity and the like with repeated use, over a long period by incorporating tantalum-doped tin oxide powder in a uppermost surface layer of the photosensitive layer and further providing excellent durability and safety.

[Name of document] Abstract[Abstract]

[Problems to be solved] To provide a photosensitive member with excellent photosensitive member characteristics such as photosensitivity and the like, which is capable of forming superior images without fogging or producing unsharp images, and which has excellent repetition characteristics and durability.

[Means to solve the problems] A photosensitive member comprising, on the uppermost surface, a layer comprising tantalum-doped tin oxide powder in a resin.

[Selected drawing] None